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(54) Polyvinylbutyral

(57) Polyvinyl butyral is prepared from
polyvinyl alcohol and butyric aldehyde

under particular reaction conditions to
obtain a product having advantageous
properties. The product is suitable for
use in intermediate layers in laminated
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ERRATUM

SPECIFICATION No. 2 007 677 A

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SPECIFICATION **Polyvinyl butyral**

The invention relates to manufacture of polyvinyl butyral, especially to a method of preparing this compound allowing control as desired of various properties which are important in the application of polyvinyl butyral in making laminated glass.

Polyvinyl butyral is frequently used as a spacer for laminated safety glasses used for example in the manufacture of windscreens for vehicles.

Polyvinyl butyral is generally obtained by a condensation reaction between butyric aldehyde and polyvinyl alcohol, the latter being itself prepared by hydrolysis of polyvinyl acetate. By varying the conditions of the reaction, the proportions of the starting compounds and the molecular weight of the polyvinyl alcohol used as well as incorporating various additives and plastifiers it is possible to vary to a very great extent the properties of the final product. Thus there have been proposed very many variants of the usual processes of preparation of polyvinyl butyral in order to modify the physico-chemical properties as a function of the intended application.

The following properties are considered important in making laminated glass (the tests used to measure them will be described below in the description):

- the flow under compression of the polyvinyl butyral sheet;

- the resistance to shock of a laminated glass comprising such a sheet of polyvinyl butyral as spacer (ball drop test);

- the force of adhesion of the polyvinyl butyral to glass sheets of the glass laminate (Pummel test);

- transparency of the laminated glass (determination of the "turbidity" of the laminate);

- resistance to moisture of the laminated glass.

Certain known processes for synthesis of polyvinyl butyral allow control of one or the other of the first four properties in this list, but there has not hitherto existed, to the knowledge of the applicants, a process allowing simultaneous modification of several of these properties and/or modification of the resistance to moisture.

Further, the plastifiers which are known to be used in the usual process are generally expensive products of which the use considerably increases the cost of the laminated glass obtained from a polyvinyl butyral thus prepared.

The present invention is intended to remedy these disadvantages of the known techniques by providing a method of preparation of polyvinyl butyral which allows modification as required of one, several or all of the properties mentioned above, and which lend itself to the use of plastifiers which are much less expensive than those in the usual technique.

According to one aspect of the invention there is provided a method of preparing polyvinyl butyral by reaction of polyvinyl alcohol in aqueous solution with butyric aldehyde, in which to an aqueous solution comprising from 8 to 15% by weight of polyvinyl alcohol, an acid catalyst and an emulsifier held between 5 and 12°C, there is introduced under agitation, butyric aldehyde in a quantity sufficient to react with from 75 to 88% of the polyvinyl alcohol in the mixture, the introduction of the butyric aldehyde being carried out progressively for a duration such that the polyvinyl butyral formed precipitates from 10 to 90 minutes after the start of this introduction, the resulting mixture is held under agitation for a duration greater than 30 minutes at a temperature of 8 to 15°C, the temperature of the mixture is then raised to a value from 60 to 80°C over a period from one hour and a half to 4 hours, there is then incorporated in the mixture a base to obtain a pH from 9 to 11, the temperature is maintained at said value for a duration greater than a quarter of an hour and the polyvinyl butyral precipitated is separated from the mixture.

Polyvinyl butyral will be referred to below as p.v.b.

The polyvinyl alcohol used as a starting material preferably has a content of acetate less than 5%.

There is preferably used as the catalyst acid hydrochloric acid, as it is relatively cheap. The acid may be used in the form of an HCl solution of density 1.18. The quantity of this solution used is preferably from 2.5 to 10% by weight of polyvinyl alcohol. The Applicants have found, in fact, that below 2.5% by weight of acid the precipitate of p.v.b. has a tendency to form a block, which complicates the operations of separation and washing of this compound. Above 10% by weight, there takes place rapid precipitation of the p.v.b. with a risk of formation en masse of the latter during precipitation.

Further, the cost of the p.v.b. increases considerably when too large a quantity of hydrochloric acid is used.

As emulsifier it is advantageous to use a dodecylbenzene sulphonate, which, in known manner, gives a p.v.b. having an acceptable turbidity. The quantity of dodecylbenzene sulphonate will represent, preferably, from 0.15 to 0.40% by weight of polyvinyl alcohol. In fact, below 0.15% by weight there is formed in the reactor at the moment of heating, a mass of p.v.b. which would appear at the end of precipitation in the absence of emulsifier. When there is used more than 0.40% by weight of dodecylbenzene sulphonate, on the weight of polyvinyl alcohol, the dodecylbenzene sulphonate tends not to be eliminated when the p.v.b. obtained is washed, which has the effect of giving a poor turbidity in the product.

There is used a quantity of butyric aldehyde sufficient to react only with 75 to 88% by weight of the polyvinyl alcohol present in the mixture, in order to give a p.v.b. having good properties of flow.

The butyric aldehyde is introduced progressively in the solution of polyvinyl alcohol, previously brought to a temperature from 5 to 12°C. The duration of introduction is preferably from 15 to 60 minutes and it is most preferably of the order of 30 minutes. It is found, in fact, that the speed of precipitation of the p.v.b. depends on the rate of introduction of butyric aldehyde and below a duration of introduction of 15 minutes, the speed of precipitation of the p.v.b. is too high, with the effect of risking formation of a mass of the latter. Above 30 minutes, the speed of precipitation is too slow, with the result of formation of pellets of p.v.b. which are difficult to wash. The duration of 30 minutes is preferred, as it corresponds to obtaining a p.v.b. powder having a good appearance, of which the granulometry is especially suitable for later treatments.

The condensation reaction which produces p.v.b. is exothermic and the temperature of the reaction mixture increases therefore to a value from 8 to 15°C, while the butyric aldehyde is introduced. The rate of introduction of butyric aldehyde should be such that, as a function of the reaction conditions and the duration of introduction of the butyric aldehyde, the p.v.b. finishes precipitation between about 10 and 90 minutes after the start of introduction of aldehyde.

After precipitation, it is preferable to leave the mixture under agitation for a duration greater than 30 minutes at the temperature of 8 to 15°C at which it was during the reaction.

The mixture is then heated progressively such as to increase its temperature to 60 to 80°C, preferably about 70°C. The increase of temperature takes place over between 1½ hours and 4 hours, preferably 2½ hours, corresponding to a temperature increase of 22°C per hour. If the final temperature is less than 60°C, the p.v.b. obtained gives diffusing laminated panes. It is the same for temperatures greater than 80°C and further, there is found formation of blocks of p.v.b. in the reactor. The final temperature of 70°C and the rise in temperature of 22°C per hour are preferred, as they lead to a p.v.b. of good appearance, of which the granulometry is well adapted to subsequent treatments.

To neutralise, at the temperature thus chosen, the acid catalyst and increase in pH of the mixture to between 9 and 11 there is advantageously used sodium hydroxide, which is less expensive than other bases and which further gives to the p.v.b. obtained mechanical properties, notably resistance to shock, at least as good as those obtained with other bases such as potassium hydroxide or calcium oxide.

After this neutralisation the mixture is maintained at the chosen temperature from 60 to 80°C for a duration which may be from 0.25 to 4 hours, then it is returned to ambient temperature.

It is possible to separate the precipitated p.v.b. by simple filtration followed by washing with deionised water, moisture extraction and drying. It is found that a single washing of the recovered precipitate gives a high turbidity in the final product and it is therefore preferable to effect at least two washings and two filtrations of the p.v.b. successively. Beyond three successive washings, the turbidity is only improved very slightly.

The Examples which will be given below will illustrate the critical character of the conditions for carrying out the process which has been mentioned.

Before describing the Examples of the invention, there will first be explained how the trials mentioned above, which allow estimation of certain characteristics of p.v.b., are carried out.

Test for flow under compression

There is used for this test a press having heatable plates.

A sample of the sheet of p.v.b., having a thickness of 0.76 mm (± 0.01 mm) is cut into a test piece in the form of a disc of 26 mm diameter. The disc is placed between two glass sheets 60 x 60 mm. The assembly is put between the plates, maintained at 125°C., of the heatable press. After 5 minutes of preheating without applying pressure the composite is subjected for 5 minutes to a pressure of 10 bars. If D represents (at close to 0.25 mm) the diameter of the disc of p.v.b. pressed, the flow is given by the formula:

$$F = \frac{D - 26}{26} \times 100$$

In general two measurements are carried out per sample.

It is considered that, for the application of p.v.b. to a glass laminate, the flow under compression should be at least equal to 60%.

Pummel test (adhesion to glass sheets)

The samples of laminated glass used in this test and the following are prepared as follows. A sheet of p.v.b. of 760 microns thickness is previously stored in humidity, placed between two glass sheets 30.5 x 30.5 cm, the laminated glass then being compressed under pressure of 10 kg/cm² at 138°C for twenty minutes. From one of these samples, there is removed, for the Pummel test, a sample 150 x 300 mm. The latter is stored for 8 hours at -18°C. This sample is then placed on an inclined support at 45° and beaten with a hammer having a flat head of 0.450 kg until the glass is pulverised. The

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surface used is about 100 × 150 mm and the blows of the hammer are distributed over the whole surface. The quantity of glass remaining adhered to the polyvinyl butyral sheet is compared on a standard "Pummel" scale marked as 0 to 10.

- 5 The trial is carried out on the two faces of the laminated glass and the result is expressed consequently by two values of the Pummel scale, determined in the following manner: 5

	% of the p.v.b. sheet surface of which the glass is unstuck on breaking	Pummel value	
	100	0	
10	95	1	10
	90	2	
	85	3	
	60	4	
	40	5	
15	20	6	15
	10	7	
	5	8	
	2	9	
	0	10	

- 20 It is considered that a laminated glass thus tested is acceptable if the two Pummel values obtained are greater than 5. 20

Falling ball test (resistance to shock)

- 25 The trial is carried out with a steel ball having a weight of 2.270 kg which is caused to fall on the central part of the sample, which is flat, of laminated glass resting in a horizontal position on a frame of wood. The sample of laminated glass measures 305 mm × 305 mm and the sheets of glass having 3 mm thickness. 25

The samples are at a temperature of 21°C (± 2°C) and the trial is carried out at increasing height of drop of a ball. There is determined the approximate height expressed in feet, for which more than 90% of the samples tested resist passage of the ball through the laminate.

- 30 This test is considered positive when this approximate height is equal to or greater than 17 feet (5.18 metres). 30

Test for determination of turbidity

The "turbidity" of a transparent sheet is defined as being the percentage of luminous flux traversing it which is diverted by an angle greater than 2.5 degrees.

- 35 The measurement of the turbidity is carried out according to Standard NF 54—111 (which corresponds largely with the method A of Standard ASTM D 1003—61). 35

For applications of p.v.b. to making of transparent glass laminates there are considered acceptable turbidity values less than or equal to 0.3%.

Test for resistance to humidity

- 40 The samples of laminated glass are prepared by interposing a plastified spacer of 762 microns thickness between two glass plates 30.5 × 30.5 × 0.30 cm. These samples are placed in boiling water for two hours and then examined to detect possible formation of bubbles or a translucent white band at the periphery of the samples. The absence of the formation of bubbles or white translucent bands indicates that the laminate has passed with success the test for humidity resistance. 40

- 45 Various examples of syntheses of polyvinyl butyral will now be described by way of illustration. In these examples, when laminated glass is referred to, there is meant a glass prepared by interposing a plastified spacer of p.v.b. stored in humidity, having a thickness of 760 microns, between two glass plates of 30.5 × 30.5 × 0.30 cm, and compressing this composite under a pressure of 10 kg/cm², at 138°C, for about 20 minutes. 45

EXAMPLE 1

Into a solution of 30 kg polyvinyl alcohol in 300 litres water at a temperature of 10°C, there is mixed 67.5 g of sodium dodecylbenzene sulphonate and 2.65 kg of hydrochloric acid of density 1.18. The mixture being maintained at a temperature of 10°C, there is introduced progressively and regularly over 30 minutes, 17.1 kg of butyric aldehyde.

There is observed an increase of temperature of several degrees.

The solution becomes white and its viscosity increases. Suddenly 28 minutes after the start of introduction of aldehyde there is observed appearance of the precipitate and a reduction in viscosity. The mixture is then left to stand for 90 minutes at a temperature of 13°C. Then the temperature is progressively increased to 70°C, the duration of increase in temperature being 150 minutes. The mixture is then neutralised with 1.35 kg of sodium hydroxide. It is held at 70°C for 240 minutes. It is then cooled and filtered. The recovered powder is washed twice, moisture extracted and dried.

The laminated glass made starting from this resin has good optical and mechanical properties and a good resistance to moisture. After having been subjected to humidity test, this laminated glass has no white coloration or turbidity at any point on the surface of the sample, including the edge of the laminate.

The trials effected on the sheet of p.v.b. made from the resin obtained give the following characteristics:

— flow under compression : 76%

— turbidity : 0.3

— drop of ball : 20 feet (6.1 m)

EXAMPLE 2

To a solution of 30 kg of polyvinyl alcohol in 300 l of water, there is mixed 135 g of sodium dodecylbenzene sulphonate and 2.65 kg of hydrochloric acid of density 1.18. The trial is carried out under the same conditions as Example 1.

The resin obtained has poor optical properties; the turbidity of the laminate is 0.6 and therefore poor.

This Example shows the unfavourable influence of a content of emulsifier greater than 0.40% by weight of the polyvinyl alcohol.

EXAMPLE 3

Example 1 is repeated with 33.75 g of sodium dodecylbenzene sulphonate instead of 67.5 g. Numerous balls form in the reactor and the resin obtained has mediocre properties, especially with regard to turbidity, which gives a non-transparent laminate which is more or less whitened. This Example shows the undesirable influence of a content of emulsifier less than 0.15% by weight of polyvinyl alcohol.

EXAMPLE 4

Example 1 is repeated up to precipitation. After holding at 13°C, the temperature is brought to 90°C. Large blocks form in the reactor and the sheet of polyvinyl butyral obtained from the recovered and treated resin has a flow of 58%. The laminate is not transparent. This Example shows the undesirable influence of heating of the reaction medium beyond 80°C after precipitation of the p.v.b.

EXAMPLE 5

There is mixed 1.5 kg of hydrochloric acid of density 1.18 and 67.5 g of sodium dodecylbenzene sulphonate in a solution of 30 kg polyvinyl alcohol in 300 litres of water. The mixture being initially at 10°C, 16.5 kg of butyric aldehyde are introduced in 30 minutes. After precipitation, the mixture is held at 13°C for 90 minutes. It is then brought to 70°C and the catalyst is neutralised. After holding for 240 minutes at 70°C the mixture is cooled and filtered. The precipitate is then washed and filtered three times, then dried.

The resin thus obtained has a turbidity of 0.3 and the laminated glass prepared from this p.v.b. has a ball fall of 19 feet, a Pummel of 9+9 and a flow of 64%. This laminate when subjected to a humidity test does not have any white coloration or any turbidity at any point.

EXAMPLE 6

Into a mixture of a solution of polyvinyl alcohol hydrochloric acid and sodium dodecylbenzene sulphonate, identical to that of Example 5, but at a temperature of 15°C, there is introduced 16.5 kg of butyric aldehyde. After precipitation and after holding of the mixture at a low temperature, the latter is heated with a rate of temperature rise of 22°C per hour. Large blocks then form in the reactor and the resin obtained gives a laminate having turbidity.

This Example shows the undesirable influence of a starting temperature for the materials greater than 12°C.

EXAMPLE 7

Example 5 is repeated with 0.5 kg of hydrochloric acid instead of 1.5 kg.

5 The resin obtained accepts badly the Flexol (registered trade mark) used as plastifier and the sheet 5 obtained exudes.

This Example shows the undesirable influence of a content of catalyst less than 2.5% by weight on the polyvinyl alcohol.

EXAMPLE 8

10 Example 5 is repeated under the same conditions, except that the maximum temperature is 50°C 10 instead of 70°C.

The resin obtained gives a turbid laminate.

This Example shows the undesirable influence of a temperature of reheating of the reaction mixture to less than 60°C after precipitation of the p.v.b.

15 EXAMPLES 9 and 10 15

Example 5 is repeated up to the first filtering of the mixture.

The resin recovered is then washed once, moisture extracted and then dried (Example 9). The turbidity of the laminate is then 0.7. The washing is thus insufficient.

When the resin is washed and filtered twice (Example 10) the turbidity is 0.4.

20 EXAMPLES 11 to 13. 20

In a solution of 10°C of 30 kg of polyvinyl alcohol of molecular weight 106,000 in 300 litres of water, there is introduced 0.75 kg of hydrochloric acid and 67.5 g of sodium dodecylbenzene sulphonate; 17.1 kg of butyric aldehyde are then added progressively in 30 minutes.

25 After precipitation, the mixture is held for 30 minutes at the temperature reached. It is then heated 25 to 65°C and neutralised with 0.405 kg of sodium hydroxide. After 30 minutes of holding 65°C, the mixture is cooled and filtered. The resin is then washed and filtered, extracted and dried.

The sheet obtained from this resin has a flow of 61%. A laminate incorporating this resin has a turbidity of 0.2, a ball fall of 23 feet and excellent resistance to humidity. It does not have any alteration after having been subjected to the humidity test.

30 This trial is repeated with a mixture of 27.5 kg of polyvinyl alcohol of molecular weight 106,000 30 and 2.6 kg of polyvinyl alcohol of molecular weight 32,000 (Example 12). The trial is carried out under the same conditions as for Example 11. The flow of the sheet made from the p.v.b. produced is 68%.

35 The trial is repeated with a mixture of 24 kg of polyvinyl alcohol of molecular weight 106,000 and 6 kg of polyvinyl alcohol of molecular weight 32,000 (Example 13). The flow of the sheet made with the 35 p.v.b. obtained is 71%.

EXAMPLES 14 to 25

These examples illustrate the effect of the duration of precipitation, which depends on the duration of introduction of the aldehyde and also the temperature of the starting products and the concentration of the acid catalyst.

40 In a first trial (Example 14), a solution of 39 kg of polyvinyl alcohol in 390 litres of water is cooled 40 to a temperature of 10°C. There is added 90 g of sodium dodecylbenzene sulphonate and 31 of hydrochloric acid of density 1.18. The mixture being at a temperature of 10°C, there is introduced progressively and regularly, in 30 minutes, 21 kg of butyric aldehyde.

45 There is observed a duration of precipitation (the duration separating the start of introduction of 45 the aldehyde from the end of the precipitation) of 28 minutes.

After precipitation, the mixture is held under agitation at the temperature reached for 1 hour 30. It is then brought to 70°C in 2 hours 50 minutes and neutralised with 18 litres of sodium hydroxide of 10% by weight concentration. After holding at 70°C, the mixture is cooled, filtered and washed. After extraction and drying of the resin obtained it is used for making a laminate of which the optical and the 50 mechanical properties are good.

Different plastifiers have been used with the resin obtained above and no exudation of a sheet of plastified p.v.b. nor incompatibility have been found with the use of Flexol (di(2 ethyl butyrate) of triethylene glycol), of Plastolein 90—83 (a mixture of C6—C9 ethylene glycol esters) and *n*-hexyl adipate, which are the least expensive plastifiers but are not normally in this technique.

55 The laminated glass incorporating such a sheet of p.v.b. withstands perfectly the humidity test 55 without any alteration (white colour, turbidity at any point in the sample, including the edges).

Example 14 is repeated (Examples 15 to 25) with a temperature of the polyvinyl alcohol solution of 5° or 10°C, a quantity of acid of 1.5, 3 or 6 litres (that is 4.5%, 9% and 18% by weight of polyvinyl alcohol), and a duration of introduction of the aldehyde of 10 to 30 minutes.

The Table below shows the conditions of these different trials and the characteristics of the p.v.b. thus prepared:

Examples	14	15	16	17	18	19	20	21	22	23	24	25
Temperature (°C)	10	10	10	10	10	10	5	5	5	5	5	5
HCl (litres)	3	3	6	6	1.5	1.5	3	3	6	6	1.5	1.5
Duration (minutes)	30	10	30	10	30	10	30	10	30	10	30	10
Precipitation time (minutes)	28	10	18	9	43	25	38	21	27	16	70	41
Presence of grains in the sheet (1)	0	+	0	+	+	++	+	+	0	+	++	++

(1) — 9 : no grain.

— + : a few grains.

— ++ : many grains.

It is found that according to the temperature of precipitation, the polyvinyl-butylal resin has variable appearance and properties.

A product precipitated too slowly has numerous grains which are retained on washing and gives badly plastified grains in the sheet.

A resin precipitated slowly gives a sheet which is less flexible than a powder precipitated rapidly.

The reaction carried out with a time of precipitation of about half an hour gives a powder of very good appearance and having good properties.

A precipitation which is too rapid gives a non-homogeneous product having however large blocks and which may possibly give a turbid laminate. This is the case with the majority of Examples made with 6 litres of acid (18% relative to the polyvinyl alcohol).

EXAMPLES 26 to 34.

These Examples illustrate the effect of the temperature of neutralisation on flow.

Example 1 is repeated with neutralisation temperatures of 70, 80 and 90°C, and durations of holding at a low temperature of 1 hour 30, 4 hours or 6 hours and durations of holding at 70°C of 1, 2 or 4 hours.

The flows of the sheets prepared from the p.v.b. thus made are measured.

The results obtained are shown in the Table below:

Neutralisation temperature	70 °C			80 °C			90 °C		
Example	26	27	28	29	30	31	32	33	34
Duration at low temperature	1h 30	4 h	6h	1h 30	4h	6h	1h 30	4h	6h
Duration at neutralisation temperature	1h	4 h	2h	2h	1h	4h	4h	2h	1h
Flow	126%	73%	77%	58%	73%	65%	58%	44%	50%

It is found that the flow of the sheet obtained is small for a neutralisation temperature of 90°C, whereas it has a good value for a neutralisation temperature of 70°C.

EXAMPLES 35 to 42

These Examples have the purpose of showing the influence of the neutralisation temperature on the properties of the resin and the sheet.

Example 1 is repeated with neutralisation temperatures of 55, 60, 65 and 70°C, the durations of holding at a low temperature after precipitation from 30 to 90 minutes, the durations of holding at a high temperature after neutralisation from 15 to 120 minutes and the quantities of hydrochloric acid of density 1.18 from 2.5% to 5% by weight with respect to the polyvinyl alcohol.

5 In the following Table are shown the conditions of these trials and the results obtained.

5

Example	Neutralisation temp.	Quantity of HCl	Duration at low temp.	Duration after neutralisation	Presence of grains in the sheet
35	55°C	3.3%	90 mn	30 mn	++ (1)
36	60°C	3.3%	30 mn	60 mn	0 (2)
37	65°C	3.3%	60 mn	15 mn	0
38	70°C	3.3%	45 mn	120 mn	0
39	55°C	2.5%	45 mn	15 mn	++
40	60°C	2.5%	60 mn	120 mn	+ (3)
41	65°C	2.5%	30 mn	30 mn	0
42	70°C	2.5%	90 mn	60 mn	0

(1) ++ : many grains.

(2) 0 : no grains

(3) + : a few grains.

EXAMPLES 43 to 50

These Examples are intended to show the influence of the duration of holding at the temperature of neutralisation after the latter.

10 Example 1 is repeated with temperature holding after neutralisation, for 15, 30, 60 and 120 minutes, the quantity of hydrochloric acid of 1.18 density being from 2.5% to 5% by weight with respect to the polyvinyl alcohol, the duration at low temperature after precipitation being from 30 to 90 minutes and the temperature of neutralisation being from 60° to 70°C.

10

The Table below show the conditions and results of these trials.

Example	Duration after neutralisation	Quantity HCl	Duration at low temperature	Temperature of neutralisation	Ball Drop test	Pummel test
43	120 mn	3.3%	45 mn	70°C	17 ft	9+9
44	120 mn	2.5%	60 mn	60°C	29 ft	9+9
45	60 mn	3.3%	30 mn	60°C	24 ft	9+9
46	60 mn	2.5%	90 mn	70°C	21 ft	8+8
47	30 mn	5%	60 mn	70°C	13 ft	9+9
48	30 mn	2.5%	30 mn	65°C	24 ft	8+9
49	15 mn	5%	90 mn	60°C	13 ft	8+8
50	15 mn	3.3%	60 mn	65°C	13 ft	9+9

The sheets of p.v.b. thus made have a humidity content close to 0.7. It is seen that the longer the duration of temperature, after neutralisation, the greater is the probability of having a good ball drop test.

EXAMPLE 51

20 There is dissolved 30 kg of polyvinyl alcohol in 300 litres of water and there is added 2.65 kg of hydrochloric acid of density 1.18 and 67.5 g of sodium dodecylbenzene sulphonate.

20

The mixture being brought to 10°C, 16.5 kg of butyric aldehyde are introduced regularly in 30 minutes.

After precipitation, the mixture is left under agitation for 90 minutes at the temperature of 13°C. This temperature is then brought to 70°C in 2 hours 15 minutes.

5 After holding for a duration of 2 hours at 70°C, the mixture is neutralised by 1.35 kg of sodium hydroxide, then held for 4 hours at 70°C. It is then cooled, filtered, washed, extracted and dried. 5

The resin obtained, plastified with a di (2 ethyl butyrate) of triethylene glycol (Flexol), or Plastolein 90—83 (a mixture of C6—C9 ethylene glycol esters) or *n*-hexyl adipate gives a sheet which does not exude.

10 No incompatibility has been observed with the three plastifiers above. 10

EXAMPLE 52

Example 14 is repeated but with 22 kg of butyric aldehyde against 21 in the case of Example 14.

The resin obtained has a content of —OH groups of 20.6% (against 22.3% in Example 14). The sheet of p.v.b. made from this resin has a flow under compression of 76% (against 67% for Example 14).

15 It is seen that the increase in the weight of aldehyde mixed with a quantity of polyvinyl alcohol improves the flow figure. 15

EXAMPLE 53

Example 1 is repeated with a quantity of hydrochloric acid of density 1.18 of 0.75 kg, the duration of holding at low temperature of 30 minutes, the duration of holding at high temperature after neutralisation of 30 minutes and a temperature of neutralisation of 65°C.

20 The resin obtained gives a sheet having no grain and having a flow of 65%. The laminated glass made with this sheet has turbidity of 0.3, a ball drop of 24 feet and a Pummel result of 8+9. 20

CLAIMS

25 1. A method of preparing polyvinyl butyral by reaction of polyvinyl alcohol in aqueous solution with butyric aldehyde, in which to an aqueous solution comprising from 8 to 15% by weight of polyvinyl alcohol, an acid catalyst and an emulsifier held between 5 and 12°C, there is introduced under agitation, butyric aldehyde in a quantity sufficient to react with from 75 to 88% of the polyvinyl alcohol in the mixture, the introduction of the butyric aldehyde being carried out progressively for a duration such that the polyvinyl butyral formed precipitates from 10 to 90 minutes after the start of this introduction, the resulting mixture is held under agitation for a duration greater than 30 minutes at a temperature of 8 to 15°C, the temperature of the mixture is then raised to a value from 60 to 80°C over a period from one hour and a half to 4 hours, there is then incorporated in the mixture a base to obtain a pH from 9 to 11, the temperature is maintained at said value for a duration greater than a quarter of an hour and the polyvinyl butyral precipitated is separated from the mixture. 30

35 2. A method according to Claim 1, in which the acid catalyst comprises hydrochloric acid. 35

3. A method according to Claim 2, in which the acid used has a density 1.18 and the quantity of acid used is at least 2.5% of the weight of polyvinyl alcohol.

4. A method according to any one of Claims 1 to 3, in which the emulsifier is a dodecylbenzene sulphonate.

40 5. A method according to Claim 4, in which the quantity of dodecylbenzene sulphonate used is 0.15 to 0.40% by weight of the polyvinyl alcohol. 40

6. A method according to any one of Claims 1 to 5, in which the duration of introduction of the butyric aldehyde is about 30 minutes.

45 7. A method according to any one of Claims 1 to 6, in which the temperature to which the reaction mixture is raised after precipitation of the polyvinyl butyral is about 70°C. 45

8. A method according to one of Claims 1 to 7, in which the duration of the rise in temperature, after precipitation of the polyvinyl butyral and holding at the precipitation temperature, is of the order of 2.5 hours.

50 9. A method according to any one of Claims 1 to 8, in which after separation, the polyvinyl butyral is washed at least twice. 50

10. A method according to any one of Claims 1 to 9, in which the polyvinyl alcohol has a content of acetate less than 5%.

11. A method of preparing polyvinyl butyral, substantially as hereinbefore described with reference to the foregoing Examples.

55 12. Polyvinyl butyral prepared by a method according to any one of Claims 1 to 11. 55

13. Laminated glass comprising a spacer layer comprising polyvinyl butyral according to Claim 12.

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